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PRELIMINARY MINERALOGICAL STUDY OF Pt-Pd-RICH SAMPLES FROM THE STILLWATER COMPLEX FOR ANACONDA COPPER COMPANY, DENVER

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PRELIMINARY MINERALOGICAL STUDY OF Pt-Pd-RICH SAMPLES FROM THE STILLWATER COMPLEX FOR ANACONDA COPPER COMPANY, DENVER

by

Louis J. Cabri* and J.H. Gilles Laflamme**

SUMMARY

The mineralogy of fractions coarser than 45 μm for four samples rich in Pt and Pd, from the Stillwater complex, Montana, was determined in a preliminary manner. Sample 360C, studied in the greatest detail, contains most of the Cu as chalcopyrite, most of the Ni as pentlandite and most of the Pt and Pd as braggite. Braggite [(Pd,Pt)S], which ranges in composition to Pt-free vysotskite, occurs as a primary mineral, but mostly as a secondary fine-grained complex intergrowth with silicates(?). This secondary braggite has not been described before and may give recovery problems. Rarer platinum-group minerals present are: Pt-Fe alloy, moncheite ($PtTe_2$), kotulskite (PdTe), temagamite (Pd_3HgTe_3), and other Pd tellurides.

Platinum-group minerals found in sample WD6 are moncheite, Pt-Fe alloy and palladian gold. Sample 345B contains primary braggite, moncheite and palladian gold while no platinum-group minerals were found in the brief microscopic reconnaisance of sample 378B.

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INTRODUCTION

Mr. R.N. Miller, Project Coordinator, Stillwater, for the Anaconda Copper Company, Denver, Colorado, enquired whether CANMET could undertake a "preliminary" mineralogical study of drill-core samples from the Stillwater complex, Montana. On November 1, 1979, it was agreed that the investigation be done in the Mineralogy Section, Physical Sciences Laboratory, and that the cost be charged to Anaconda Copper Company, but that CANMET would reserve the right to publish any mineralogical data resulting from the work. The contract would include:

1. Sample preparation for four samples.
2. Polished sections for the four samples.
3. Mineralogical study of the ore minerals for at least one sample.
4. A report.

SAMPLES

Four high-grade drill-core samples from the Anaconda Company's zone of interest were received for this study. Their description and assay results were provided in a letter of 15 July, 1979, by Mr. Steve Barnes. The distribution of sulphides within the core was reported as extremely inhomogeneous and agreement between assays of duplicate samples from the same interval has not been very good. Basic data for the samples is summarized in Table 1. The location of the diamond drill holes was not provided by Anaconda.

TABLE 1. ANALYTICAL DATA (IN PPM) FOR DRILL-CORE SAMPLES

Hole	Footage	Weight	Ni	Cu	Pt	Pd	Au
360C	515.5-516.5	435g	1,500	126	51.5	165.0	2.175
345B	370.5-371.5	410g	138	119	10.75	43.1	1.200
378B	1136-1138	610g	67	3.7	7.25	13.925	0.04
WD6	133-134	115g	470	260	15.52	56.65	1.72

The Stillwater complex has been actively explored for platinum-group elements (PGE) for the last twelve years. The differentiated sequence of layered mafic and ultramafic igneous rocks comprising the Stillwater complex are briefly reviewed by Conn (1979) who also describes exploration for PGE. Earlier studies on the platinum-group mineralogy are also briefly described by Conn and, more recently, the Pt-Pd tellurides by Cabri et al. (1979).

SAMPLE PREPARATION AND METHODS OF INVESTIGATION

After removal of small slices to provide polished sections of uncrushed material, the samples were crushed to 150 μm (minus 100-mesh) and then screened into four fractions: minus 150 μm plus 106 μm (minus 100 plus 150-mesh), minus 106 μm plus 75 μm (minus 150 plus 200-mesh), minus 75 μm plus 45 μm (minus 200 plus 325-mesh) and minus 45 μm (minus 325-mesh). The three coarser fractions were subjected to gravity separations in a separatory funnel using liquids of 2.96 and 3.3 specific gravity as tabulated in Table 2.

TABLE 2. PRIMARY SEPARATION OF SAMPLES

Sample	Mesh (μm)	wt. g.	Float 2.96	Sink 2.96	Float 3.3	Sink 3.3	% Sink 3.3
WD6	-150+106	21.325	9.089	12.047	6.158	5.864	6.6
	-106+75	17.030	7.109	9.652	5.813	3.781	4.2
	-75+45	13.573	8.414	5.016	4.280	0.616	0.7
	-45	37.425	-	-	-	-	-
360C	-150+106	74.798	69.921	3.920	2.758	1.065	0.3
	-106+75	49.443	46.864	1.716	1.162	0.507	0.15
	-75+45	45.516	43.571	1.376	1.026	0.341	0.10
	-45	161.955	-	-	-	-	-
345B	-150+106	81.035	27.204	53.794	28.693	24.699	7.0
	-106+75	60.887	20.428	40.382	30.249	9.619	2.7
	-75+45	56.130	10.525	45.574	42.358	2.885	0.8
	-45	152.910	-	-	-	-	-
378B	-150+106	123.128	78.693	45.389	13.241	31.924	5.7
	-106+75	102.170	63.306	38.217	27.541	10.340	1.8
	-75+45	56.330	33.277	22.961	21.495	1.270	0.2
	-45	277.530	-	-	-	-	-

The sink fractions were separated into magnetic and non-magnetic portions and were then subjected to further gravity separation with an elutriation tube using a liquid of 3.3 specific gravity as described by Cabri and Laflamme (1976). Except for sample 378B, there was an insufficient quantity of the magnetic portion to warrent further gravity separation, as shown by the results in Table 3. Likewise, the finest fractions for samples WD6 and 360C had insufficient material and, instead of further separations,

TABLE 3. SECONDARY SEPARATION OF THE SAMPLES*

Sample	Mesh (μm)	Mag.	Non-Mag.	Float	1st Sink	2nd Sink	3rd Sink	% Sink**
WD6	-150+106	0.155	5.708	5.44	0.09	0.09	0.08	0.29
	-106+75	0.195	3.585	3.26	0.07	0.10	0.09	0.29
	-75+45	0.144	0.472	-	-	-	-	-
360C	-150+106	0.170	0.962	0.69	0.06	0.06	0.11	0.07
	-106+75	0.074	0.433	-	-	-	-	-
	-75+45	0.062	0.278	-	-	-	-	-
345B	-150+106	0.027	24.653	24.0	0.14	0.20	0.20	0.15
	-106+75	0.015	9.582	9.12	0.09	0.09	0.11	0.08
	-75+45	0.010	2.844	2.57	0.04	0.07	0.10	0.06
378B	-150+106	2.11	-	1.94	0.17	-	-	0.03
	-106+75	1.54	-	1.43	0.10	-	-	0.018
	-75+45	0.555	-	0.51	0.04	-	-	0.007
	-150+106	-	29.81	29.27	0.07	0.06	0.07	0.04
	-106+75	-	8.77	8.40	0.05	0.07	0.11	0.04
	-75+45	-	0.706	0.47	0.12	0.10	-	0.04

*all weights in g; **of total sample

these were split to provide enough material for three polished sections each. The ideal weight of material in this size range, in order to produce a monolayer in an ~3 cm diameter polished section, is about 0.1 g. These separations produced sufficient material for twelve polished sections for all samples except for sample 378B for which there was only enough concentrate for eleven sections.

All the polished sections for sample 360C were studied by ore microscopy while only two sections for each of the remaining samples was so examined. The identity of platinum-group minerals (PGM) was confirmed by qualitative electron-probe analyses using an energy dispersive system (EDS) and standards. Quantitative analyses were performed on braggite and vysotskite using the standards and X-ray lines reported by Cabri et al. (1978). A scanning electron microscope (SEM) was used to resolve some of the complex fine intergrowths and back scattered electron (BSE) photomicrographs were obtained.

MINERALOGY

1. Sample 360C

The principal opaque minerals in the non-magnetic portions of this sample, in decreasing order of abundance, are pyrite, pentlandite, chalcopyrite and braggite series [(Pd,Pt,Ni)S], with minor millerite and ilmenite. The rarer minerals are Pt-Fe alloys, moncheite ($PtTe_2$), kotulskite (PdTe), temagamite(Pd_3HgTe_3), other Pd tellurides and arsenopyrite. In the magnetic fractions, magnetite is most abundant, followed by pyrrhotite and then by all the same sulphides occurring in the non-magnetic fractions, but in lesser amounts. Shards of iron from the crushing operations are also common in the magnetic fraction.

Pyrite is the most abundant opaque mineral and appears to have crystallized later than the other sulphides. It occurs as coarse-grained aggregates, up to a few millimeters in diameter, scattered in altered silicates (Fig. 1). A lesser quantity of pyrite occurs as finer-grained boxwork-like intergrowths associated with Fe-Ni-Cu sulphides (Fig. 2). Chalcopyrite, pentlandite and pyrrhotite occur as intercummulus remnants exhibiting different degrees of alteration or replacement by secondary

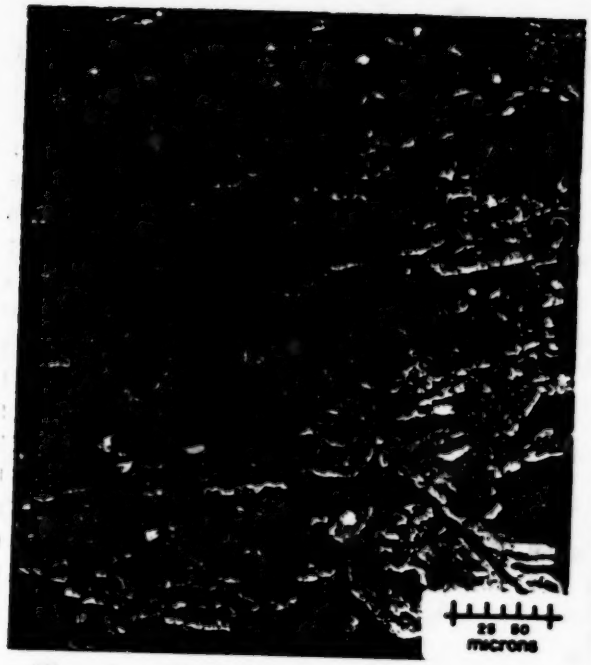

Fig. 1. Photomicrograph of coarse-grained pyrite aggregate with silicate inclusions (black). 360C-2.

Fig. 2. Fine-grained secondary pyrite replacing pyrrhotite in silicates. SEM BSE image. 360C-1.

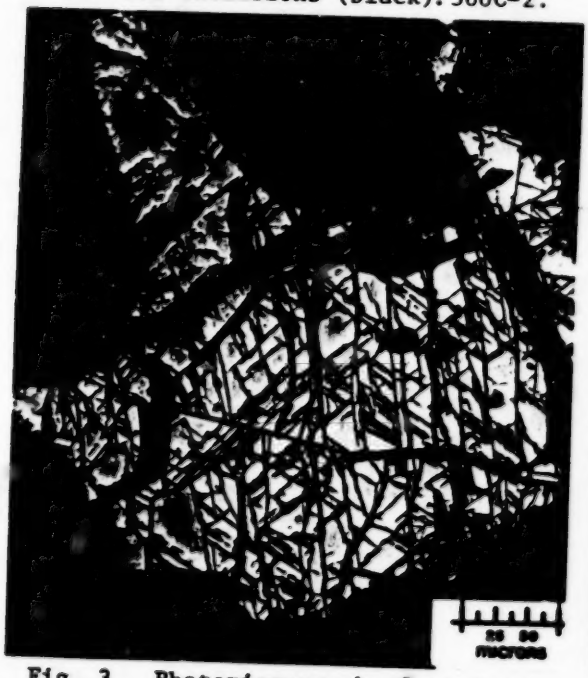

Fig. 3. Photomicrograph of typical pentlandite-chalcopyrite (not readily visible) intercummulus remnant in silicates. 360C-2.

Fig. 4. SEM photomicrograph of intercummulus sulphides in silicates. Dark grey pentlandite with inclusions of braggite (white) associated with coarser braggite set in a matrix of "altered" braggite. BSE image.

silicates (Fig. 3 and 4). These sulphides also occur disseminated as a fine dust within certain silicates, with some apparent remobilization into veins (Fig. 5). Millerite occurs as fine-grained intergrowths within pentlandite, sometimes also associated with braggite (Fig. 6).

The platinum-group minerals (PGM) are closely associated with chalcopyrite and pentlandite. The braggite series is as abundant or slightly less abundant than chalcopyrite and ranges in composition from (Pt,Pd)S to PdS (Cabri et al. 1978). Two randomly selected grains with "high" and "low" Pt gave the following compositions, by quantitative probe analysis: $(Pd_{0.59}Pt_{0.34}Ni_{.06})S_{1.01}$ = braggite and $(Pd_{0.76}Ni_{0.23})S_{1.01}$ = vysotskite. The braggite series was found to occur over a range of sizes with very variable characteristics. It occurs as coarse millimeter-size aggregates to very fine micron-size intergrowths (Fig. 6, 7 and 8). A large number, if not the majority, of the minerals described as braggite series in this sample consist of complex, fine-grained intergrowths which may represent a stage of alteration. These "altered" areas have a dull, weathered appearance which does not take a good polish. Examination of the finer details with the SEM revealed inhomogeneities in element distribution with Pt-rich "reaction rims" surrounding normal-looking braggite (Fig. 9). The "altered" braggite appears to be replacing pentlandite while the crystallization history of the "normal" braggite may rather be related to the primary sulphide magmatic history (Fig. 9). EDS spectra of the "altered" or secondary braggite revealed some Fe, Si and Al, besides Pt, Pd and S, therefore suggesting a very fine-grained Pt-Pd sulphide-silicate mixture.

Braggite is a very important PGM in the Merensky reef, but its composition has not been reported to extend to that of vysotskite there. Vysotskite was first reported as a minor mineral of secondary origin in the

Fig. 5. Photomicrograph of altered silicate with dust-like sulphide disseminations and remobilized sulphide veins. 360C-2.

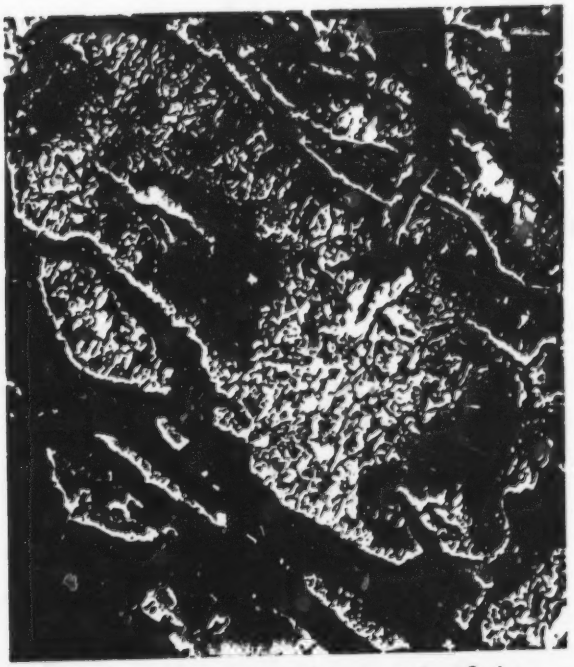

Fig. 6. SEM photomicrograph of irregular millerite (light grey) and braggite (white) inclusions in pentlandite-chalcopyrite. BSE image 360C-2.

Fig. 7. SEM photomicrograph of fine braggite oriented intergrowth (white) similar to dark grey chalcopyrite in pentlandite. BSE image, 360C-2.

Fig. 8. SEM photomicrograph of coarse braggite with darker areas showing irregular nature of fine-grained braggite-silicate(?) mixture, BSE image, 360C-2.

Noril'sk deposits by Genkin and Zvyagintsev (1962). Braggite and vysotskite are the most abundant PGM in a sulphide-rich horizon of the banded zone of the Stillwater complex (Conn 1979) as well as in the PGE mineralization at Lac des Iles, Ontario (Cabri and Laflamme 1979). The secondary braggite, in the form found in sample 360C has not, however, been described from any of the deposits cited above.

The other PGM are very much less abundant than braggite and consist of Pt-Fe alloy and Pt and Pd tellurides. They vary in size from a few microns to a maximum of about 40 microns and are always found included in primary pentlandite, chalcopyrite or braggite. The Pt-Fe alloy (Fig. 10) was compared to standards with the EDS and is probably of Pt_3Fe composition. Moncheite ($PtTe_2$) and kotulskite (PdTe) are not uncommon PGE tellurides (Cabri et al.

Fig. 9. SEM photomicrograph showing detail of "altered" braggite replacing pentlandite (dark grey) and speckled white (high Pt) "reaction rim" around "normal" braggite. BSE image, 360C(-106+75 μm).

Fig. 10. SEM photomicrograph of Pt-Fe alloy inclusion in braggite, itself included in chalcopyrite. BSE image, 360C(-75+45 μm).

1979), but temagamite (Pd_3HgTe_3) is much rarer (Fig. 11); this being the second documented occurrence, world-wide. Other tellurides, as yet unidentified, need further detailed study.

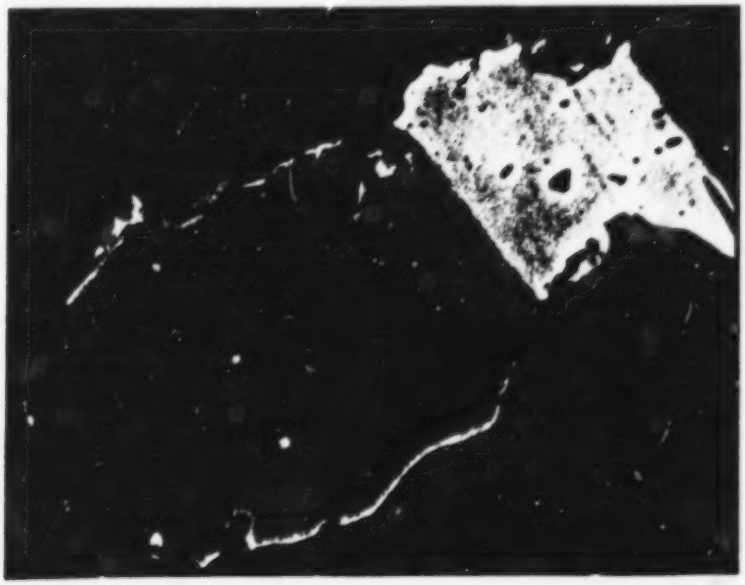

Fig. 11. SEM photomicrograph of complex intergrowth of temagamite with moncheite (white) and kotulskite (dark grey) in pentlandite (black). BSE image, 360C (-106+75 µm).

Most of the sulphides are liberated in the minus 75 plus 45 µm fraction. Chalcopyrite appears to have the largest proportion of liberated grains free of inclusions in contrast to pentlandite which often contains chalcopyrite, silicate and pyrrhotite inclusions at that size. Much of the pyrite also has inclusions of silicates. The braggite is found attached to other sulphides but is also often free at that size. However, most grains consist of the secondary braggite-silicate(?) mixture alone or with primary braggite. The other PGM are not only less abundant, but are also finer grained and thus mostly occur as inclusions or attached grains. The fraction less than 45 µm, though a significant proportion of the crushed products, was not examined.

2. Sample WD6

A rapid reconnaisance of two sections revealed that this sample consists of primary blebs, up to one cm in length, of chalcopyrite-pentlandite-pyrrhotite with minor magnetite as well as disseminations in altered silicates and along veins and fractures. As in sample 360C, secondary aggregates of pyrite occur, but in lesser quantity, as well as a few disseminations of sphalerite in chalcopyrite. Cubanite also occurs in chalcopyrite, often as well-developed laths. No braggite was found, only small inclusions of moncheite, Pt-Fe alloy and palladian gold (Cabri and Laflamme 1974) in Cu-Fe-Ni sulphides. Pt-Fe alloy, in contrast to its occurrence as inclusions in braggite as in sample 360C, occurs as disseminations in pentlandite or chalcopyrite, sometimes as euhedral crystals (Fig. 12 and 13).

Fig. 12. SEM photomicrograph of euhedral aggregates of Pt-Fe alloy included in pentlandite-pyrrhotite. BSE image, WD6(-106+75 μm).

Fig. 13. SEM photomicrograph of very fine-grained Pt-Fe alloy disseminations in chalcopyrite. BSE image, WD6(-106+75 μm).

3. Sample 345B

Microscopic examination of two sections revealed that this sample contains aggregates of Cu-Fe-Ni sulphides ranging up to a cm in diameter and is also veined and replaced by pyrite. The secondary pyrite has developed into well-formed crystals in some areas and is in contrast with an apparent primary pyrite associated with pentlandite-chalcopyrite-pyrrhotite. Minor alteration to marcasite is also present and minor magnetite occurs. The PGM consist mainly of braggite, which is fresh-looking and unaltered, in addition to minor moncheite and palladian gold.

4. Sample 378B

A very brief microscopic review of two sections showed that sulphides are very sparsely distributed as a few remnants of primary chalcopyrite-pentlandite-pyrrhotite-cubanite, secondary pyrite and some arsenopyrite. Chromite and magnetite may be more abundant than sulphides, and the latter also occurs as a secondary mineral. No PGM were found in this brief microscopic reconnaisance.

CONCLUSIONS

1. The opaque minerals in sample 360C are pyrite, pentlandite, chalcopyrite, braggite, magnetite and pyrrhotite with minor millerite and ilmenite. Rarer minerals are Pt-Fe alloys, moncheite, kotulskite, temagamite, other Pd tellurides and arsenopyrite.

2. Sample 360C contains both primary and secondary mineralization which may have occurred during metamorphism.

3. It is estimated that most of the Pt and Pd values in PGM occur as braggite. A small proportion of the Pt and Pd may occur as a solid solution in pentlandite, but this was not confirmed.

4. The secondary or altered braggite has not been reported in the literature and may cause recovery problems. It may behave differently during flotation and may also be subject to further weathering and leaching in ore dumps.

5. Rapid reconnaisance of samples WD6, 345B and 378B suggests that they are all different in PGM and sulphide assemblages.

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